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Complexes of 1-Alkyl-4-aza-1-azoniabicyclo[2.2.2]octane Bromides with Lanthanum Nitrate. Micelle-Forming and Adsorption Properties

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Abstract—Novel organometallic surfactants were synthesized from monoquaternized 1,4-diazabicyclo[2.2.2]-octanes of varied hydrophobicity [Alk = C_nH_{2n+1}, n = 14, 18] and lanthanum nitrates. The spectral, micelle-forming, and adsorption properties of the synthesized compounds were studied by IR, ^{1}H NMR and electronic spectroscopy, tensiometry, conductometry, and potentiometry. The critical micelle concentrations, counterionic micellar binding constants, and adsorption parameters at the water–air interface were determined and compared with the respective characteristics of the ligands and conventional amphiphiles.

Keywords: monoquaternized 1,4-diazabicyclo[2.2.2]octane, complex, surfactant, aggregation, adsorption

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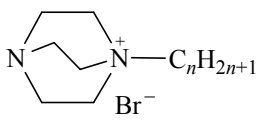
Introduction of functional chemical substituents (including metals) and biochemical fragments in amphiphilic compounds gives new types of surfactants with potentially useful physicochemical properties and, consequently, a broader range of practical applications [1–4]. The synthesis and study of such surfactants is one the most important fields of supramolecular chemistry and design of biomimetic compositions. Metal-containing surfactants offer a lot of practical opportunities. They are applied as catalysts in a great variety of chemical processes, in the synthesis of mesoporous materials and colloid synthesis of nanoparticles, as well as in medicine [4–6].

Here we report the synthesis and physicochemical study of novel metal-containing surfactants on the basis of 1-alkyl-4-aza-1-azoniabicyclo[2.2.2]octane bromides [Alk = C_nH_{2n+1}, n = 14 (**1**), 18 (**2**)] and lanthanum nitrate.



n = 14 (**1**), 18 (**2**).

The choice as ligands of monoquaternized 1,4-diazabicyclo[2.2.2]octanes bearing a long-chain substituent on the quaternary nitrogen atom was motivated by high functional characteristics of such derivatives, specifically, high aggregative, catalytic, solubilizing, and biological activities [7–9]. The presence in such bicyclic compounds of a tertiary nitrogen bridgehead atom makes possible complex formation with metals. All this opens up perspectives for the synthesis of novel amphiphilic compounds capable of forming supramolecular ensembles with a high polyfunctional activity.

The synthesis of metal complexes from ligands **1** and **2** and lanthanum(III) nitrate was performed in methanol. The structure and composition of the synthesized metal-containing surfactants were confirmed by IR and ^{1}H NMR spectroscopy and elemental analysis. The ligand:metal ratios in complexes **3** and **4** were found to be 1 : 1 and 2 : 1, respectively.

Complex formation produced radical changes in the IR spectra. In the region of stretching and deformation vibrations of the N–C bonds of the bicycle about